Polymer Blend Proton Exchange Membranes

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Objective

Develop new membranes based on polymer blends for operation at temperatures of 120°C or higher

Budget

DOE Funding FY04 = $ 95,000

Technical Barriers and Targets

DOE Technical Barriers For Fuel Cell Components

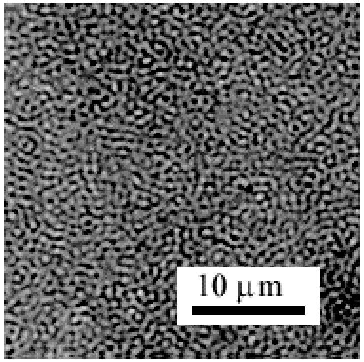
O. Stack Material and Manufacturing Costs
P. Durability
R. Thermal and Water

DOE TechnicalTargets for Membranes (Automotive) for 2005

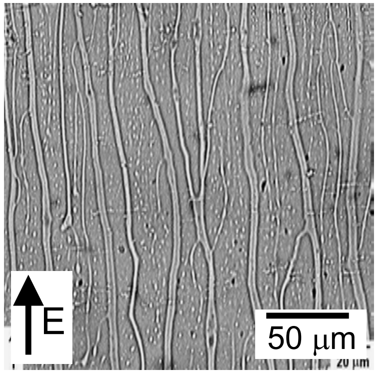
- Membrane conductivity (operating temperature) ~ 0.1 S/cm
- Operating temperature $\geq$ 120°C
- Membrane cost ~ $50/kW
- Membrane durability > 4000 h
- Hydrogen/oxygen cross-over (MEA) ~ 5 mA/cm^2
- Survivability ~ -20 °C

Approach

Develop high temperature PEMs with controlled morphology using acid-base polymer blends



1. Thermodynamics: develop a percolated ionic pathway at the interface of a spinodal morphology of a polymer blend comprising a sulfonated polyketone and a polyimide or similar second component



2. Electro-dynamics: Orient a dispersed phase of the conductive sulfo-polyketone in a polyimide matrix by applying an electric field during membrane casting

Project Safety

- Handling and disposing of SO_3: normal handling procedures for strong acids; disposal by neutralization
- Handling of hydrogen: normal handling procedures of high-pressure gas; high-flow-rate ventilation
- Handling and disposing of solvents: normal OSHA/EPA procedures used

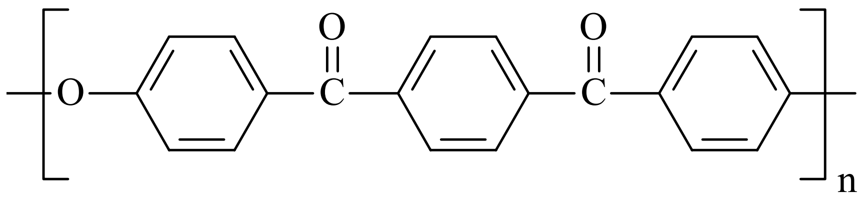
Project Timeline

10/02 – 10/03	10/03 – 10/04	10/04 – 12/06
Phase I	**Phase II**	**Phase III**
1 2	3 4 5	6 7

- Phase I: Feasibility
  1 Optimize preparation of sulfonated PEKK (SPEKK) ionomers
  2 Prepare/Evaluate SPEKK/polyether imide (PEI) blend membranes
- Phase II: Morphology Development
  3 Develop spinodal structure for SPEKK/PEI membranes and characterize membrane performance
  4 Develop procedure for orienting SPEKK/PEI membranes and characterize membrane performance
  5 MEA production and testing
- Phase III: System Optimization
  6 Optimize membrane composition and morphology for high temperature SPEKK/PEI PEM
  7 Design and evaluate other blend PEMs

Technical Accomplishments/Progress

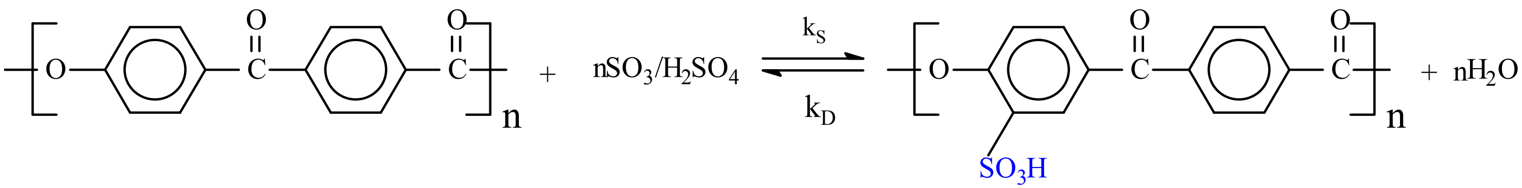
Developed Membranes Based on Poly(ether ketone ketone)

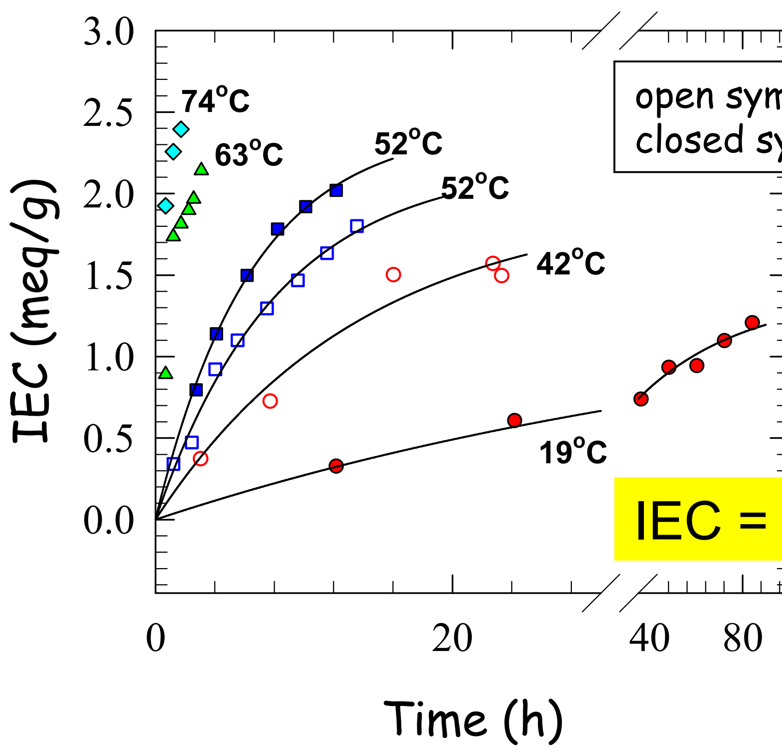


- High temperature stability (T_g ~ 155°C; T_m ~ 360°C)
- Excellent mechanical properties (engineering thermoplastic)
- Excellent chemical and solvent resistance
- Excellent oxidative stability
- Adequate resistance to desulfonation

Technical Accomplishments/Progress

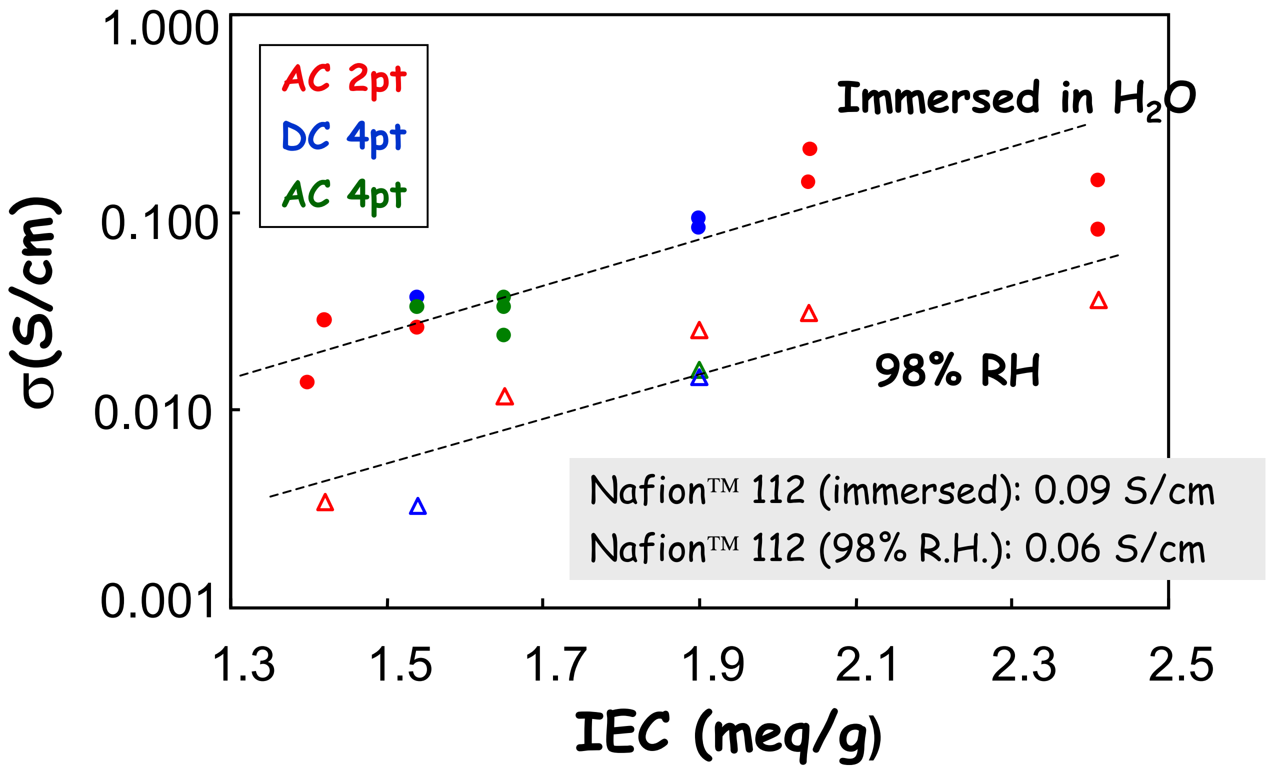
Optimized procedure for preparing sulfonated PEKK (SPEKK)





$$IEC = IEC_{\infty}[1-\exp(-t/\tau)]$$

Proton Conductivity of SPEKK



SPEKKs:

- For IEC ~ 1.8 – 2.1 meq/g, conductivity ~ 10^{-1} S/cm
- Water insoluble when IEC < 2.3 meq/g
- 20-150 μm membranes can be cast from NMP or DMAc

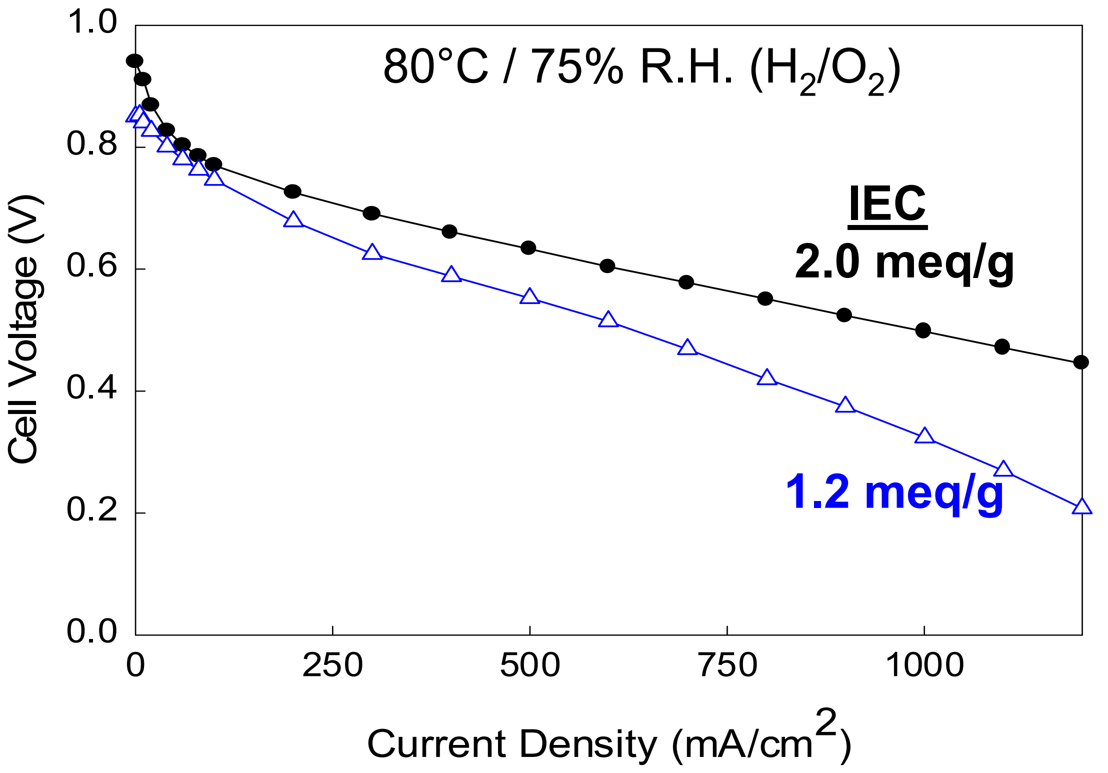
Methanol Crossover for SPEKK in MEA

	Resistance (ohm cm^2) (H_2/O_2, 80 °C)	Methanol Crossover (A/cm^2) (1M MeOH, 80 °C)
SPEKK (1.8 meq/g)	0.07	0.22
Nafion™	0.05	0.40

SPEKK membranes:

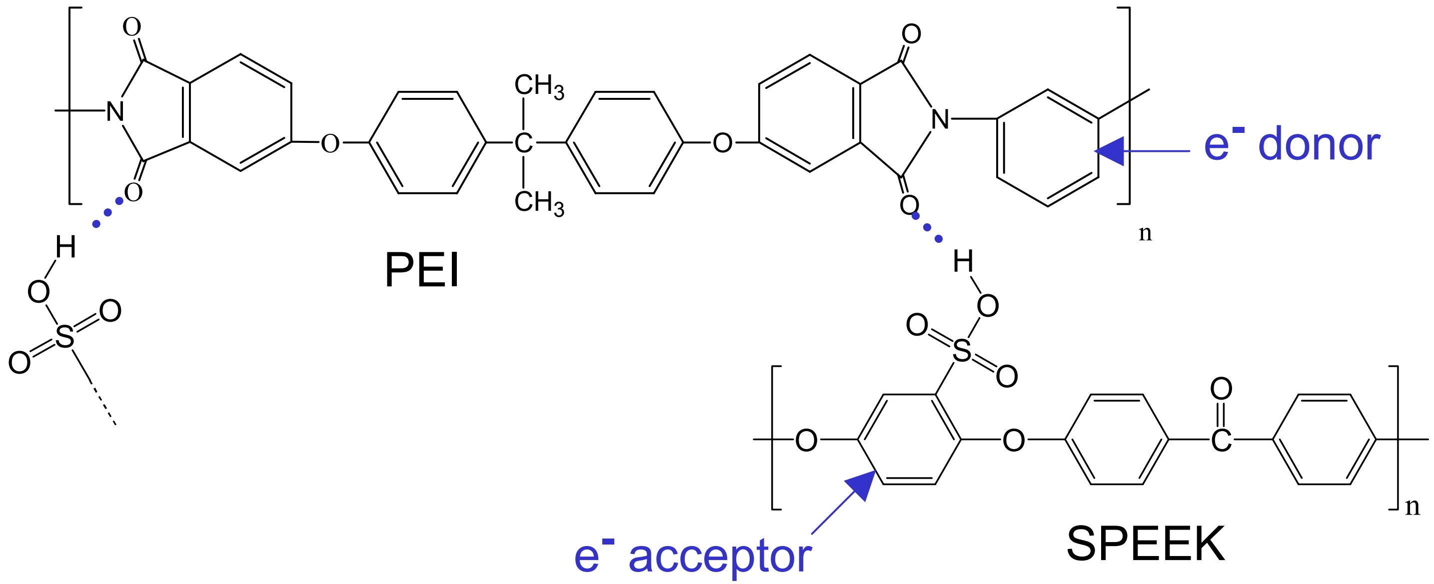
- Good proton conductivity (~ 0.1 S/cm)
- Improved methanol permeability resistance vs. Nafion™

MEA Performance of SPEKK PEMs



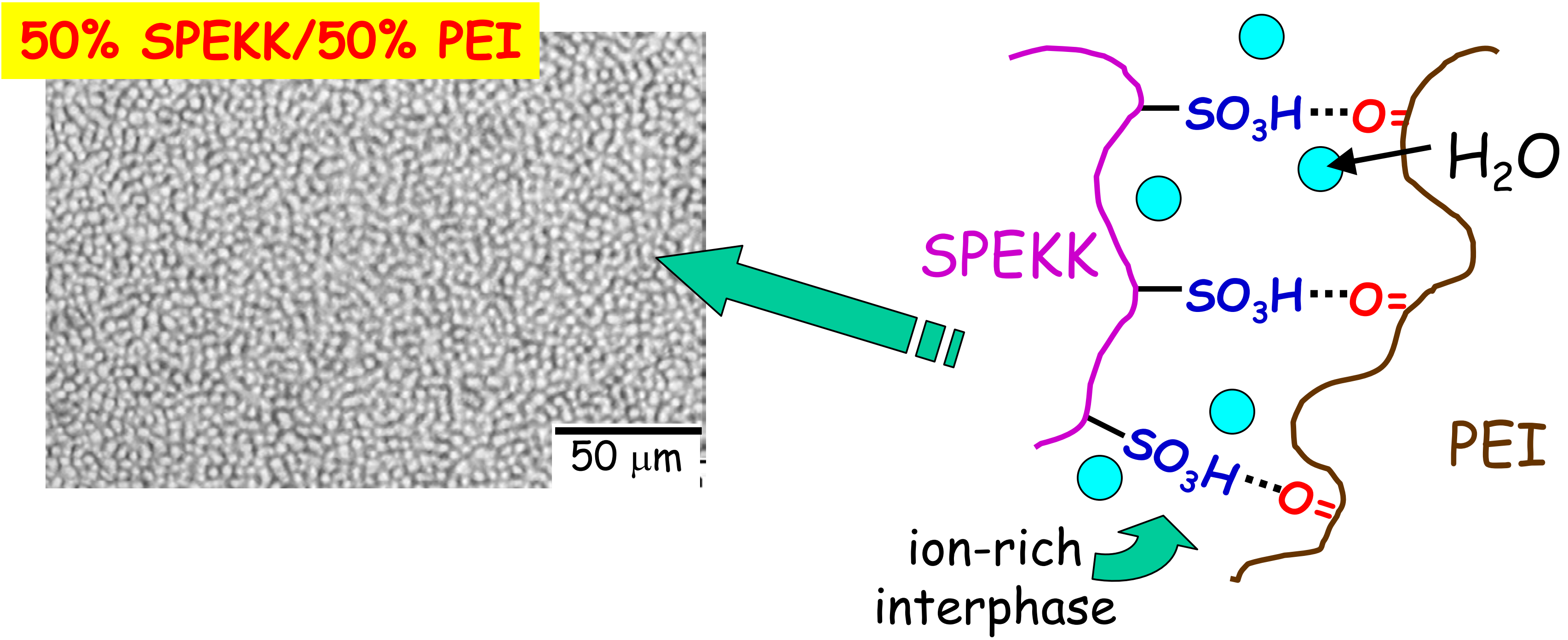
Reasonably good MEA performance

Blends of SPEKK with Poly(ether imide) (PEI)



- Strong H-bonding interactions are expected
- Ionomer provides acid groups for proton conductivity
- Relatively hydrophobic PEI provides mechanical integrity

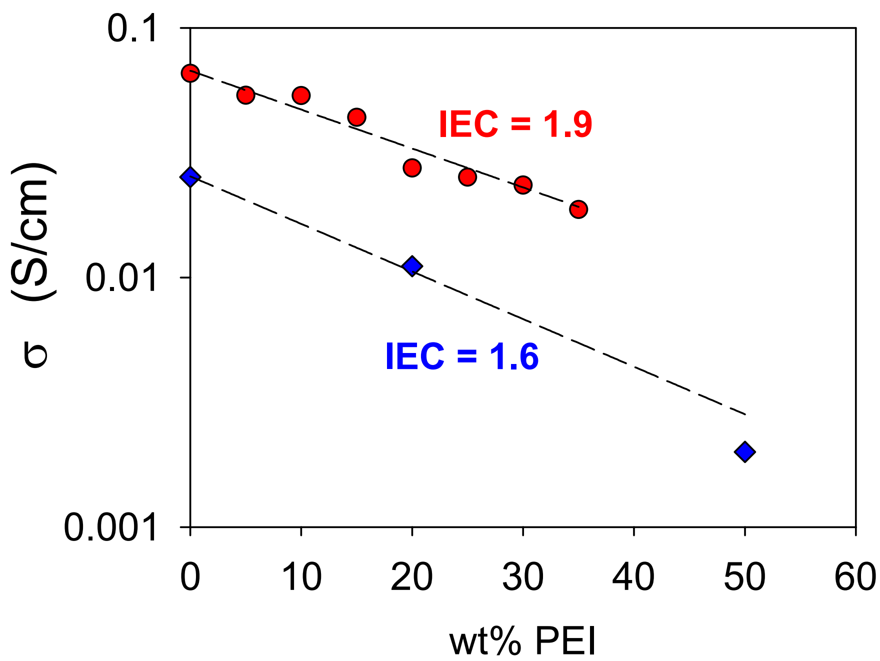
SPEKK/PEI Blend PEMs



Hypotheses:

- Ion-rich interphase provides pathway for proton conductivity
- Percolated conductive path present before water is added
- Amount of water required for conductivity will be less than for conventional ionomer membrane

Effect of PEI content on conductivity (RT)

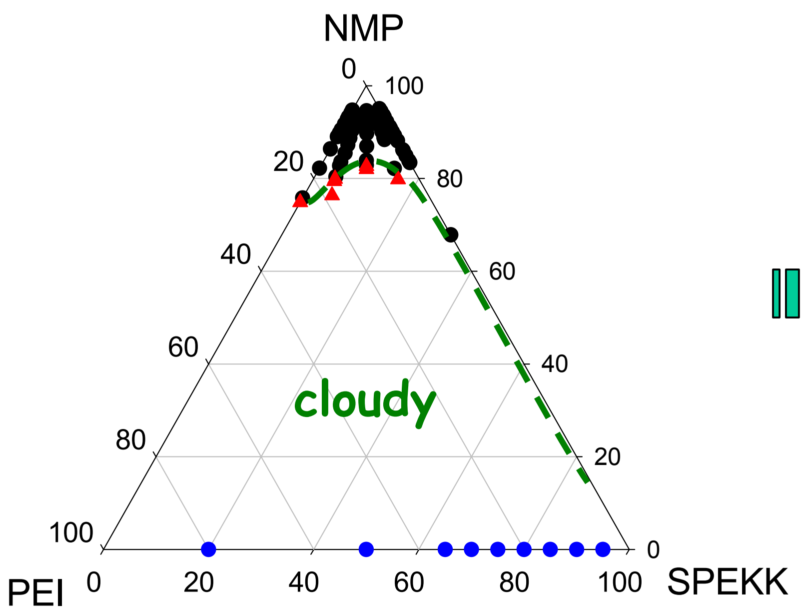


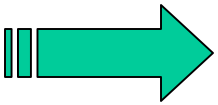
Increasing PEI concentration:

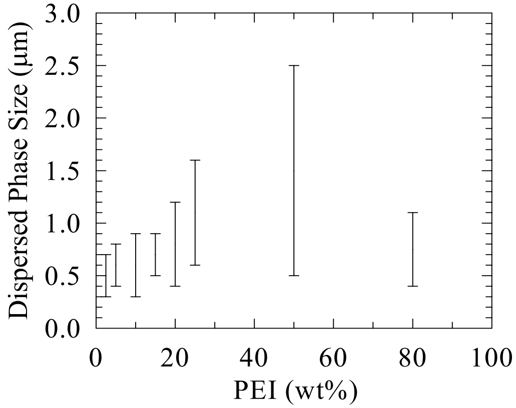
- Lowers conductivity (but still > 0.01 S/cm for c_{PEI} < 30%
- Reduces water concentration
- Improves mechanical properties of wet membrane

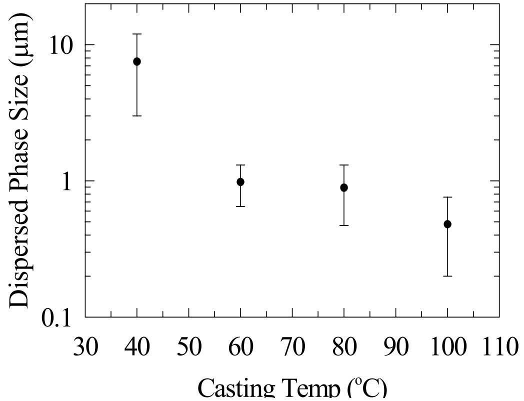
Controlling the Blend Morphology: Film Casting T

Ternary Phase Diagram



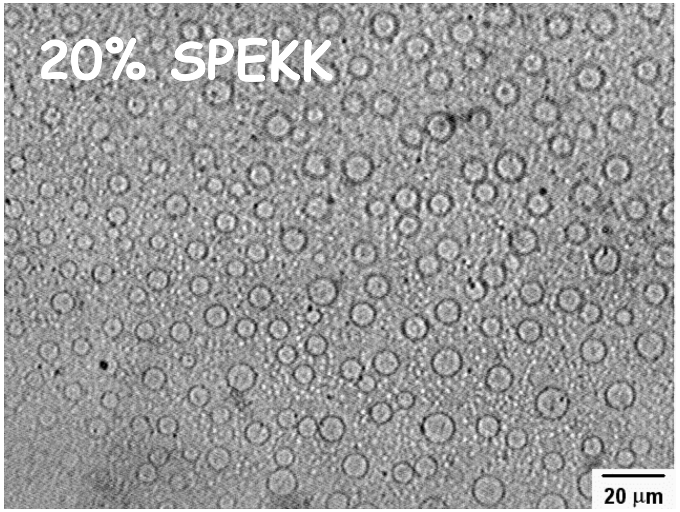




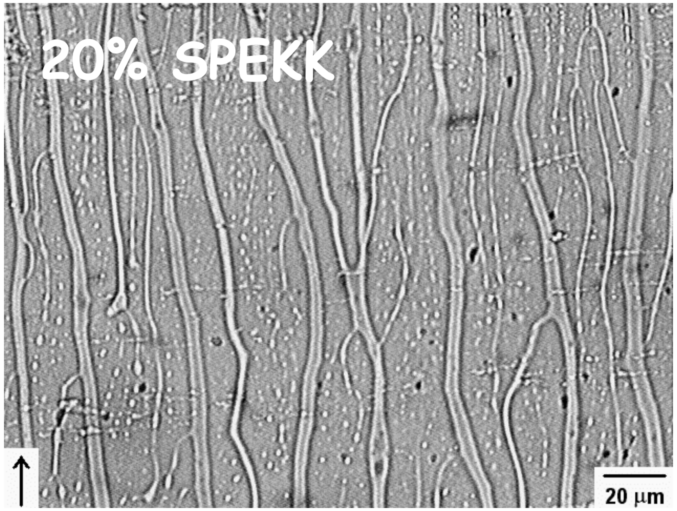


- Dispersed phase size decreases with casting temperature
- Dispersed phase size increases with increasing PEI

Controlling the Blend Morphology: Electric Field Alignment



Cast without Electric Field

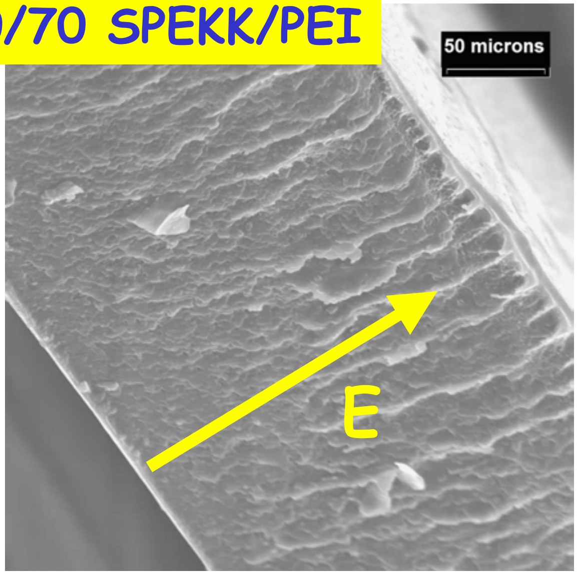


Cast with Electric Field
E = 0.5 kV/cm; f = 20 Hz

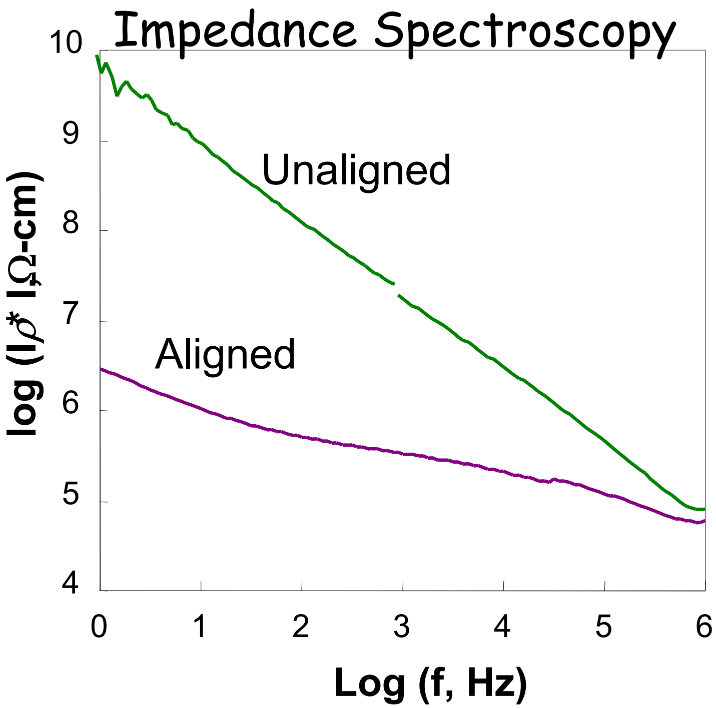
SPEKK dispersed phase can be oriented by applying an AC electric field across the membrane during processing (solution or melt)

Controlling the Blend Morphology: Electric Field Alignment

30/70 SPEKK/PEI



Oriented at 200°C;
E = 10 kV/cm; f = 20 Hz



Electric field alignment of SPEKK phase significantly increases the membrane conductivty

Interactions and Collaborations

Oxford Performance Materials (OPM): SPEKK development and blend membrane development; MEA fabrication and testing

Leveraging Resources:

Agency	Dates	Award	Outputs/Objectives
Connecticut Innovations, Inc. (UConn and OPM)	1999-01	$375K	Development of sulfonated PEKK. Initial evaluation of sulfonated PEKK for PEM fuel cell applications.
Connecticut Innovations, Inc. (UConn and OPM)	2001-03	$375K	Development of reproducible process for sulfonation of PEKK. Demonstrated feasibility of SPEKK PEMs for direct methanol fuel cells.
DOE Inventions & Innovations (OPM)	2003-05	$250K	Ongoing: sPEKK and sPEKK blend based MEAs. (subcontract to UConn)
DOE (UConn)	2003-05	$191K	Ongoing: Development of methods for controlling domain structure of polymer blends for PEM applications using thermodynamics and electric fields
Connecticut Global Fuel Cell Center (UConn)	2003-04	$75K	Development of equipment for electric field orientation of polymer films during film preparation
NSF (UConn)	1994-02	$1.1M	Fundamental studies of the thermodynamics of ionomer blends

Future Plans

Remainder of FY 2004:

- Develop ternary phase diagrams for SPEKK/PEI/solvent, using different solvents
- Produce membranes with spinodal structure
- Optimize equipment and procedures for electric field orientation of membranes
- Fabricate MEAs with controlled morphology blend membranes